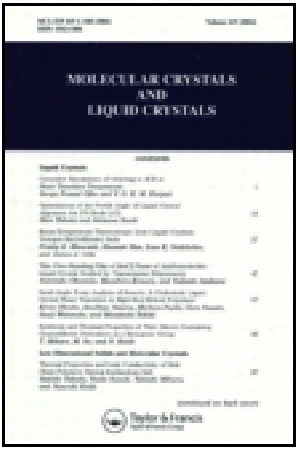

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The Mesophase Behavior and Structure of 1,1-Bis(Perfluoroalkyl)-2-Vinylcyclopropane Polymers

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We introduced new poly(2-vinylcyclopropane)s carrying two perfluoroalkyl mesogens per repeat unit at the same main chain carbon atom. The relative lengths of the hydrocarbon-fluorocarbon segments were varied. Copolymers with a non-mesogenic 2-vinylcyclopropane were also prepared. X-ray diffraction studies proved the formation of smectic mesophases, the type of which depended on the chemical nature of the polymers: SmB_2, SmI_2 (or SmF_2), and SmA_d. We emphasize the role of intramolecular microphase segregation in determining the mesophase behavior and structure.

Keywords: fluorinated polymer; microphase segregation; perfluorinated mesogen; smectic mesophase; vinylcyclopropane

INTRODUCTION

Liquid crystalline polymers having perfluorinated chain segments as side groups can form thin films in which the mesogens self-assemble in an orientationally ordered array at the polymer-air interface [1]. This surface structure appears to be mediated by the bulk mesophase

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order [2] which in contrast is not common for amorphous fluorinated polymers [3]. In this context, poly(2-vinylcyclopropane)s carrying a perfluorinated mesogen per repeat unit have proved to organize spontaneously in the bulk *and* at the surface, thereby creating a nanostructured low-energy surface [4].

Furthermore, the multifunctional character of the 2-vinylcyclopropane monomers having two substituents in the 1,1-positions makes them suitable for incorporation into a new type of polymers possessing two mesogenic groups per repeat unit [5]. Examples of such polymer structures are comparatively very few and are usually prepared by more demanding polymerization procedures than the free radical polymerization [6–8].

In this work we prepared a set of novel liquid crystalline poly(2-vinylcyclopropane)s carrying two perfluoroalkyl mesogens per repeat unit and investigated their thermotropic behavior by X-ray diffraction. We emphasize the role of microphase segregation in affecting their smectic behavior.

EXPERIMENTAL PART

Synthesis

2-(Perfluorohexyl)ethanol ($m = 2$, $n = 6$) and 2-(perfluorooctyl)ethanol ($m = 2$, $n = 8$) were used as received from Fluorochem. 4-(Perfluorooctyl)butanol ($m = 4$, $n = 8$) was synthesized according to literature [9].

Monomer **II**, 1,1-di(ethyloxycarbonyl)-2-vinylcyclopropane, was prepared following a literature procedure [10].

The syntheses of monomer **I-2,8** and the corresponding polymer p(**I-2,8**) are described here in detail as typical examples.

Monomer **I-2,8**. 19.30 g (91 mmol) of **II** was suspended with 18.92 g (330 mmol) of KOH in 20 ml of water under inert atmosphere. The mixture was stirred at room temperature for 24 h and then acidified with 36% HCl to pH = 2–3 and washed with diethyl ether. The organic layer was dried over Na_2SO_4 and evaporated under vacuum giving pure dicarboxylic acid **2**(yield 80%): m.p. 105–107°C; ^{1}H NMR (DMSO-d_6): δ(ppm) = 1.4 (2H, CH_2), 2.4 (1H, CH), 5.1–5.5 (3H, $CH_2{=}CH$), 10.6 (2H, COOH).

Then, 0.60 g (3.9 mmol) of **2**, 0.10 g (0.7 mmol) of pyrrolidinopyridine (PPy), 3.54 g (7.6 mmol) of 2-(perfluorooctyl)ethanol were dissolved in 25 ml of anhydrous CH_2Cl_2 and 5 ml of anhydrous THF at room temperature. A solution of 1.57 g (7.6 mmol) of dicyclohexylcarbodiimide (DCC) in 15 ml of anhydrous CH_2Cl_2 was then slowly added and the mixture was let to react for an additional 3 days. The organic solution was washed with 5% HCl, 5% $NaHCO_3$, water and dried over Na_2SO_4. After evaporation of the solvent, the crude product was purified by liquid chromatography on a silica gel column with ethyl acetate/hexane (1/4 v/v) as the eluent. Pure monomer **I-2,8** was obtained as a white wax (yield 66%).

FT-IR (liquid film): $\bar{\nu}\,(\mathrm{cm}^{-1}) = 3094$ (ν C–H vinyl), 2920–2860 (ν C–H aliphatic), 1732 (ν C=O), 1640 (ν C=C), 1250–1117 (ν C(O)–O, ν C–F), 658 (ωCF_2).

^1H NMR ($CDCl_3$): δ ppm = 1.6–1.8 (2H, CH_2 cyclopropane), 2.5 (5H, $CH_2CF_2 + CH$ cyclopropane), 2.6 (1H, CH cyclopropane), 4.4 (4H, $COOCH_2$), 5.1–5.5 (3H, $CH_2 = CH$).

*Polymer p(**I-2,8**).* 0.53 g (0.5 mmol) of monomer **I-2,8** and 6 mg (0.04 mmol) of azobis(isobutyronitrile) (AIBN) were introduced into a pyrex vial under nitrogen atmosphere. After 3 freeze-thaw pump cycles the vial was sealed under vacuum and the polymerization was let to proceed for 19 h at 65°C. The polymer was purified by repeated precipitations from Cl_2FCCF_2Cl solutions into methanol, and dried under vacuum. The final polymer p(**I-2,8**) was obtained as a white powder (yield 78%).

FT-IR (polymer film): $\bar{\nu}\,(\mathrm{cm}^{-1}) = 2959$–2850 ($\nu$ C–H aliphatic), 1737 (ν C=O), 1203–1082 (νC(O)–O, ν C–F), 659 (ωCF_2).

^1H NMR (trifluorotoluene): δ ppm = 2.0–3.0 ppm (8.5H, $CH_2CH{=}CHCH_2$ + cyclobutane + CH_2CF_2), 4.4 (4H, $COOCH_2$), 5.5 (1.5H, CH=CH).

^{19}F NMR (trifluorotoluene/$CDCl_3$): δ ppm from CF_3CO_2H = –12 (3 F, CF_3), –47 (2F, CF_2CH_2), –54 to –57 (5CF_2), –59 (2 F, CF_2CF_3).

Characterization

The ^1H, ^{13}C, and ^{19}F NMR spectra were recorded with a Varian Gemini VXR 300 spectrometer (operating at 299.9, 75.4, and 282.2 MHz, respectively). Chemical shifts were referenced to external TMS, unless specified otherwise.

DSC measurements were carried out with a Mettler DSC-30 instrument (10°C/min scanning rate) that had been calibrated using tin, indium and zinc standard samples. The clearing temperature (T_i) was taken as the maximum temperature in the DSC enthalpic peak of the second heating cycle. The glass transition temperature (T_g) was set at the half-devitrification temperature.

X-ray diffraction experiments were performed on powder samples with a pinhole camera under vacuum at various temperatures (±1°C) up to T_i. Ni-filtered CuK α beam ($\lambda = 1.54$ Å) was used. Several exposures were recorded so as to measure the strongest and weakest x orders of reflections on the smectic layers. Experimental amplitudes a_x were corrected for the Lorentz-polarization factor and normalized to the strongest one.

RESULTS AND DISCUSSION

A set of novel poly(2-vinylcyclopropane)s was prepared that contained two fluorinated mesogens as lateral substituents at the same chain position of the repeat unit (Fig. 1). In designing these polymer structures we introduced side groups where the relative lengths of the fluorocarbon rodlike segment ($n = 6$ or 8) and the hydrocarbon spacer segment ($m = 2$ or 4) were varied. Accordingly, the fluorinated monomers will be denoted as **I-m,n**, and the relevant polymers as p(**I-m,n**) after the numbers of CH_2 and CF_2 moieties in their side groups, respectively.

It is known [11] that perfluorinated chain segments of greater aspect ratio favor the onset of smectic mesophases in various classes of polymers; on the other hand, more flexible hydrocarbon chain spacers increase conformational freedom and segregation. Thus, we aimed at finely tuning the formation of mesophases over a wide temperature range on a chemical ground.

The reaction scheme followed for the synthesis of the fluorinated monomers **I-m,n** starting from diethyl malonate (**1**) is depicted in Figure 2. This method was relatively facile and versatile, in that it additionally yielded intermediate **II** that could then be used as a non-mesogenic monomer in subsequent copolymerization experiments for one further chemical modification of p(**I-2,8**) to give copolymers p(**I-2,8-co-II**)a–c (Fig. 1). An alternative, more straightforward procedure (also shown in Fig. 2) involved the synthesis of bisfluorinated malonates **4** in the first step. However, the eventual monomers were difficult to purify accurately and were obtained in lower reaction yields, and this synthetic pathway was not optimized.

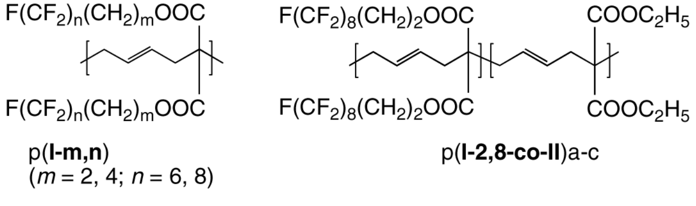

FIGURE 1 Structures of the homopolymers p(**I-m,n**) and copolymers p(**I-2, 8-co-II**)a–c (for clarity the linear repeat units are shown only).

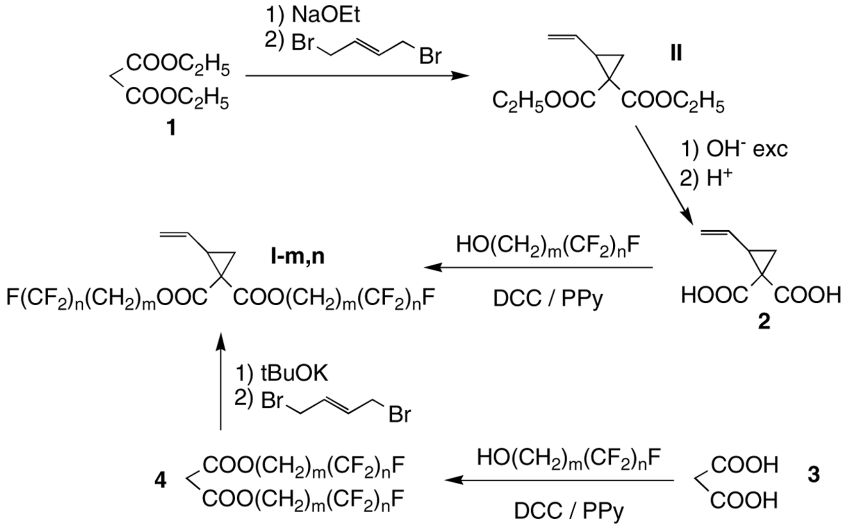

FIGURE 2 Reaction schemes for the synthesis of the 2-vinylcyclopropanes **I-m,n** and **II**.

The polymerization experiments were performed by free radical polymerization (AIBN, 60–65°C) in either bulk or trifluorotoluene solution (yields 70–85%). The copolymers were extracted with acetone that is a selective solvent for p(**II**). No sizeable amounts of polymeric products were isolated in the acetone extracts, consistent with the formation of copolymers comprised of both reacted monomers in a random fashion. The polymers were soluble in fluorinated solvents, with the exceptions of the copolymers with higher contents of non-fluorinated units that could be dissolved in common solvents for characterization. Their SEC analysis provided values of $M_n = 38000$–$45000\,g/mol$ and $M_w/M_n = 2.0$–2.2.

The free radical homopolymerization of 2-vinylcyclopropanes carrying electron-withdrawing substituents in the 1,1-positions (X and Y in Fig. 3) may involve the introduction of both linear ring-opened units and cyclic ring-closed units into an actual copolymer structure

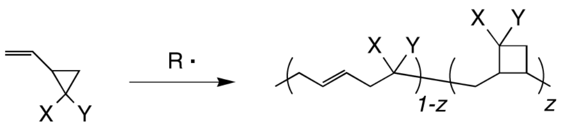

FIGURE 3 Structure of a poly(2-vinylcyclopropane) with both linear and cyclic repeat units (X, Y: electron-withdrawing groups).

[12,13]. The relative proportion of the two isomer repeat units depends, for given experimental polymerization conditions, on the steric hindrance and electronic configuration of the substituents X and Y, with bulkier groups being better accommodated in the 1,5-ring-opened linear repeat unit [14].

In accord with previous results [13,14] we found that the linear unit was incorporated principally, albeit not exclusively, in the homopolymerization experiments, e.g., up to 75% content in p(**I-2,8**). The predominance of the linear repeat units is illustrated in the simplified structures of the polymers in Figure 1. The precise influence of the configurational features of the main chain on the polymer properties is difficult to investigate and remains to be ascertained.

Each of the polymers formed one smectic mesophase (Tables 1 and 2). The clearing temperature increased with the length of the perfluoroalkyl segment (T_i from 98°C to 129°C), while it was depressed by the longer hydrocarbon spacer (down to 96°C). The glass transition temperature was little affected by the structural variations ($T_g \sim 40$–50°C), and therefore the range of mesophase existence was maximized for p(**I-2,8**) ($T_i - T_g = 86$°C). This mesogenic character was preserved in the copolymers with non-fluorinated monomer **II** for which T_i was located in the range of 150–180°C (Table 2).

This essential insensitivity of T_i to chemical composition is in marked contrast to what is observed in customary random copolymers when the mesophase-isotropic transition temperature normally drops in a substantial way with increasing content of non-mesogenic units. However, it is not surprising for copolymers based on monomers carrying long perfluorinated side groups [15]. It is assumed that strong intramolecular phase segregation confines the incompatible hydrocarbon and fluorocarbon constituents into individual smectic sub-layers. This ordered array would be less affected by chemical composition than in a totally mixed distribution of mesogenic and non-mesogenic units [16]. The details of the structure and packing of the smectic mesophase depend on the chemical features in a more subtle way than is simply anticipated by inspection of T_i.

TABLE 1 Thermal Properties of Polymers p(**I-n,p**)

Polymer	T_g (°C)	T_i (°C)	ΔH_i (J/g)
p(**I-2,6**)	40	98	5.6
p(**I-2,8**)	43	129	8.3
p(**I-4,8**)	52	96	8.3

TABLE 2 Thermal Properties of Copolymers p(**I-2,8-co-II**)a–c

Polymer	**I-2,8** (mol%)	T_g (°C)	T_i (°C)	ΔH_i (J/g)
p(**I-2,8**)	100	43	129	8.3
p(**I-2,8-co-II**)a	65	44	156	8.1
p(**I-2,8-co-II**)b	44	46	161	8.9
p(**I-2,8-co-II**)c	23	32	153	6.5
p(**II**)	0	33	–	–

We investigated the mesophase behavior by X-ray diffraction in order to identify the nature of the smectic mesophases and their structural parameters and to confirm the phase segregation of incompatible components. The detected physical parameters of the smectic phases are collected in Table 3, where they are also compared with the maximal lengths calculated by the CPK models for smectic bilayer (L_2) and monolayer (L_1) spacings.

The homopolymers gave rise to a pseudo-hexagonal mesophase (side of the hexagon $b_H = 5.7$ Å) (Fig. 4) with a layer periodicity d typical of a double layer structure ($d \gg L_1$). While the mesophase of p(**I-2,6**) was orthogonal (SmB_2, $d > L_2$), the mesophase of p(**I-2,8**) and p(**I-4,8**) was tilted (SmI_2 (or SmF_2), $d < L_2$) [17]. The respective tilt angles β of 15° and 21° were unaffected by temperature variations over the entire mesophase range. In these two last polymers, the longer perfluorooctyl chain segments were inclined to the smectic layer normal in order to fill space effectively. In both cases the average surface area S per side group was in fact too small ($S \sim 28$ Å^2) to allow interdigitation of the bulky perfluorinated chains.

TABLE 3 Structural Parameters of the Smectic Mesophases (for symbols, see text)

Polymer	d (±0.2 Å)	b_H (Å)	S (Å^2)	β (±2°)	L_2 (±1 Å)	L_1 (±1 Å)	Mesophase
p(**I-2,6**)	31.9	5.7	28	0	28	16	SmB_2
p(**I-2,8**)	32.3	5.7	28	15	34	19	SmI_2 (SmF_2)
p(**I-4,8**)	36.1	5.7	28	21	39	22	SmI_2 (SmF_2)
p(**I-2,8-co-II**)a	33.3	5.8	29	0	34	19	SmB_2
p(**I-2,8-co-II**)b	24.9	5.5[a]	30[b]	0	34	19	SmA_d
p(**I-2,8-co-II**)c	24.1	5.5[a]	30[b]	0	34	19	SmA_d

[a] Intermolecular distance.

[b] Based on a square lattice.

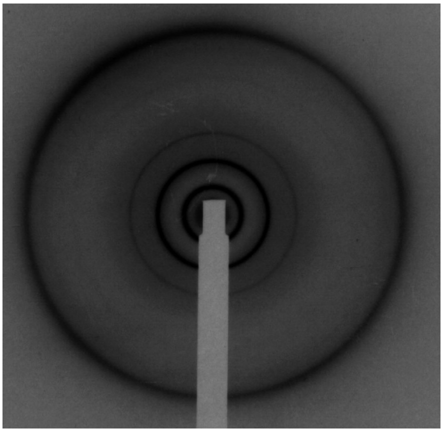

FIGURE 4 X-ray diffraction pattern of the SmI_2 (or SmF_2) phase of p(**I-2,8**) at 80°C.

The structure of the mesophase in the copolymers p(**I-2,8-co-II**)a–c depended critically on their chemical composition (Table 3). While it was a bilayer and high order (SmB_2, $d \sim L_2$) for the copolymer p(**I-2,8-co-II**)a containing a lower amount of non-mesogenic units, the mesophase was partly interdigitated and low order (SmA_d, $L_1 < d < L_2$) in the two copolymers having larger contents of such units (Fig. 5). Dilution of the perfluorooctyl side groups along the macromolecular chain gradually disrupted their in-plane order and enabled partial overlap within the

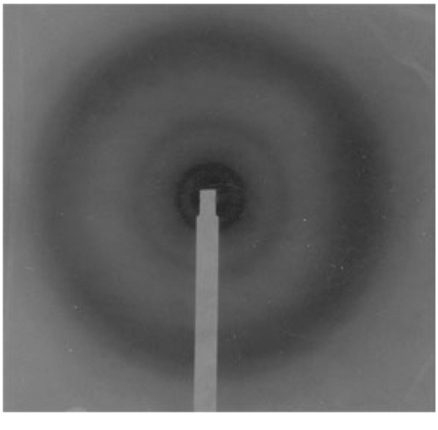

FIGURE 5 X-ray diffraction pattern of the SmA_d phase of p(**I-2,8-co-II**)b at 100°C.

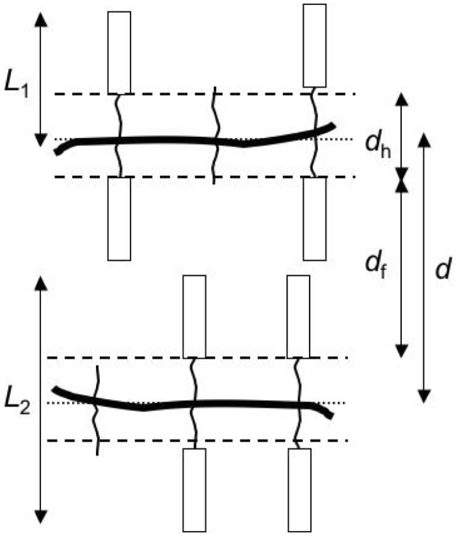

FIGURE 6 Schematic of the microphase segregated structure of the smectic phase of copolymer p(**I-2,8-co-II**)a with fluorocarbon (d_f) and hydrocarbon (d_h) sub-layers.

layers ($S \sim 30$ Å^2). Nonetheless, an effective microphase segregation operated in the copolymer rich in mesogenic units (Fig. 6).

Further insight into the structure of the smectic mesophase was gained by analysis of the small angle diffraction region. In fact the diagrams of the homopolymers and copolymer p(**I-2,8-co-II**)a presented three orders of Bragg reflections on the smectic layer planes. The normalized amplitudes a_x of the layer reflections are collected in Table 4. In the other two copolymers with lower contents of **I-2,8** units the higher harmonic reflections were either too weak to be measured with reliability or not detected. Taking into account the symmetry of

TABLE 4 Normalized Amplitudes a_x of the Smectic Layer Reflections

Polymer	a_1	a_2	a_3
p(**I-2,6**)	1	0.76	0.41
p(**I-2,8**)	1	0.69	0.38
p(**I-4,8**)	1	0.72	0.42
p(**I-2,8-co-II**)a	1	0.70	0.39

the smectic structure, the electron density profile, or its projection, $\rho(z)$ along the layer normal is given [18] by:

$$\rho(z) = \Sigma[a_x \cos(x2\pi z/d)] \tag{1}$$

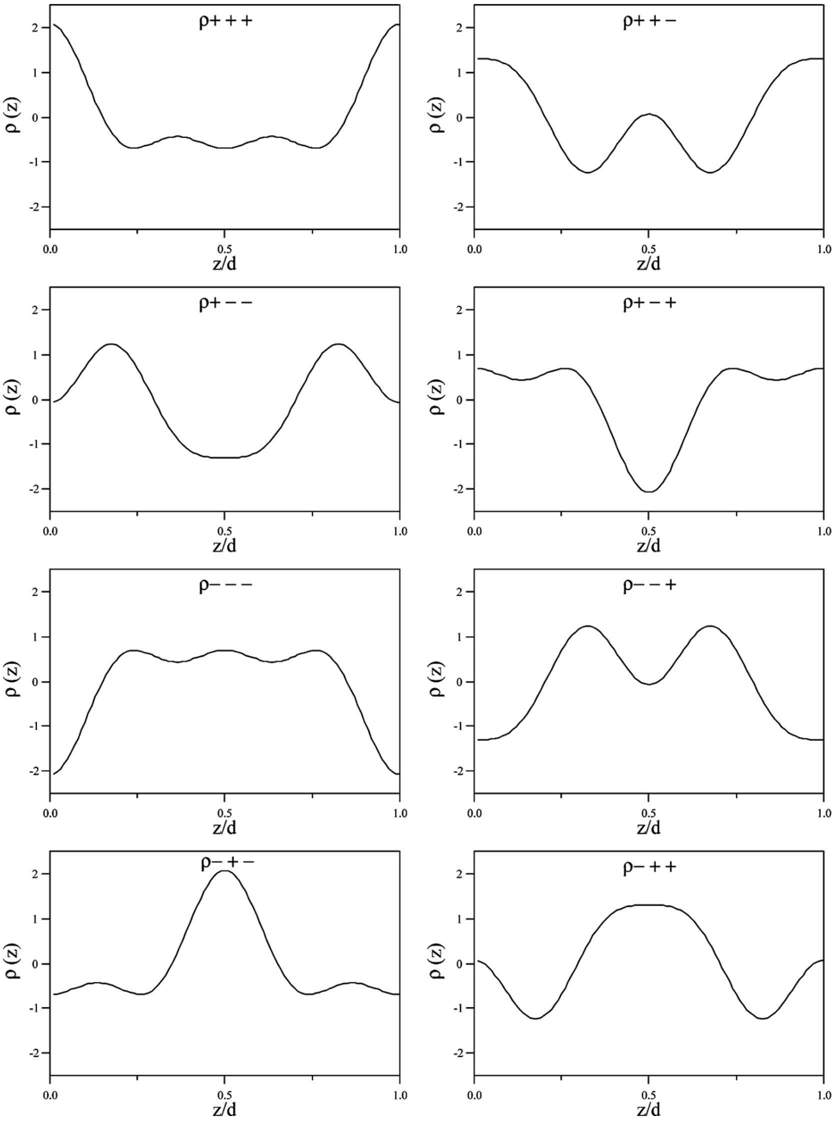

FIGURE 7 Electron density profiles for the smectic mesophase of p(**I-2,8**).

For x reflections at small angles, there are 2^x combinations of signs or electron density profiles [19]. This is illustrated for p(**I-2,8**) in Figure 7. The profile ρ_{-++} was more physically acceptable because it exhibits an absolute maximum in correspondence of the fluorocarbon side groups ($z/d \sim 0.3$–0.7) and secondary comparatively weak maxima for the hydrocarbon main chains ($z/d = 0$ and 1). The central maximum in $\rho(z)$ does not seem to be sufficiently intense to account for interdigitation of the fluorinated chains. On the other hand, the unusually high electron density for the polymer chains reflects the large number of chain carbon atoms per repeat unit. It also provides further supporting evidence of microphase segregation within the smectic layers.

Analogous considerations apply to the rest of the polymer samples investigated here for which very similar a_x values were evaluated. Thus, only minor details of their $\rho(z)$ were affected in the microphase segregated smectic structures. One significant difference is that the interlayer correlation was shorter in the copolymers with lower contents of mesogenic units, probably because of a more blurred interface.

CONCLUSIONS

The poly(2-vinylcylopropane)s carrying fluorinated side groups ($n \geq 6$) present smectic mesophases irrespective of essentially any other structural feature, including chemical composition of the copolymers with non-mesogenic components. Such inherent smectogenic tendency was enhanced owing to the concomitant presence of two fluorinated chain segments per repeat unit, that are phase segregated from the hydrocarbon backbone and spacer segments.

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